Role of Surface Structure in the Phase Separation of the Binary Electron-Hole Liquid

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Microscopic calculations are presented of the surface and interface structure of the binary electron-hole liquid in $\langle 111 \rangle$-stressed Ge at $T = 0$. The separation of the electron-hole droplet into two coexisting phases is found to have a surface precursor. The phase separation is predicted to occur without any nucleation process or hysteresis effects even though the phase transition is first order. Perfect wetting between the two liquid phases is predicted. Experimental implications are discussed.

In recent years considerable progress has been made in understanding phenomenologically the physics of the interfaces between the coexisting phases of multicomponent fluids.[1] However, the interfaces in degenerate multicomponent Coulomb Fermi liquids have not been studied at all, although the simplicity of the interactions in these systems presents a unique opportunity for accurate microscopic calculations, and recent theoretical work suggests that these liquids should have rich and interesting phase diagrams.[2] In this Letter I report on the surfaces and interfaces occurring in such a system—the electron-hole liquid (EHL) containing two different electron species (the "hot" and "cold" electrons), which is realized experimentally in $\langle 111 \rangle$-stressed Ge.[3] At $T = 0$, for suitable values of stress, and concentrations of hot electrons in the EHL which are not too high, this EHL has been predicted to separate into two phases.[2] One phase (phase I) consists of cold electrons and holes only while the other (phase II) contains hot electrons, cold electrons, and holes. At higher hot-electron concentrations the EHL consists of a single phase containing all three species. Experimental observation of this phase separation has been reported in both photoluminescence[4] and plasmon absorption[5] studies. The calculations reported here reveal that the structure of the EHL surface plays a key role in the phase separation process. An unexpected result with important experimental implications is that the phase separation should proceed without any nucleation process taking place, so long as the EHL has a free surface. This is so despite the fact that the phase transition is first order.

The present calculations are based on the density-functional formalism of Hohenberg and Kohn (HK).[6] The application of this formalism to simple electron-hole liquids has been reviewed by Rice.[7] If one assumes local charge neutrality (a good approximation for EHL surfaces) the HK energy functional at $T = 0$ takes the form

$$E[\{n_i\}] = \int \left[g_0(\{n_i(\vec{r})\}) + \sum_{i\nu} g_2{}^{i\nu} |\nabla_\nu n_i|^2 \right] d^3r, \quad (1)$$

where i stands for hot electrons (h), cold electrons (c), or holes (H), n_i is the density of species i, and ν labels principal axes. The local approximation g_0 to the energy density consists of kinetic and exchange-correlation energy contributions which are calculated as in Ref. 2. For electrons the coefficient $g_2{}^{i\nu}$ of the first gradient correction to the kinetic energy is given by $g_2{}^{i\nu} = \hbar^2/72 n_i m_{i\nu}$ where $m_{i\nu}$ is the longitudinal ($\nu = l$) or transverse ($\nu = t$) mass. For holes $g_2{}^{H\nu}$ is calculated numerically from the random-phase-approximation static dielectric function in the $\vec{k} \cdot \vec{p}$ formalism,[8] extending to nonzero stress the work of Reinecke et al.[9] Since the anisotropy of the EHL surface tension is small, isotropic approximations are commonly used for the simple EHL. Following Ref. 9, I define $g_2{}^i$ by $3g_2{}^i = g_2{}^{il} + 2g_2{}^{it}$ and use $g_2{}^i$ in place of $g_2{}^{i\nu}$ in (1). The problem of minimizing E to find the surface profiles n_i is then handled by solving numerically the Euler equations

$$\partial g_0/\partial n_j - dg_2{}^j/dn_j (dn_j/dz)^2 - dg_2{}^H/dn_H (dn_H/dz)^2 - 2g_2{}^j d^2n_j/dz^2 - 2g_2{}^H d^2n_H/dz^2 = \mu_j, \quad (2)$$

where j stands for h or c, μ_j is the bulk pair chemical potential, z is the coordinate normal to the surface, and the partial derivatives are taken keeping $n_H = n_h + n_c$. The surface or interface tension is

given by

$$\sigma = \int_{-\infty}^{+\infty} dz [g_0(\{n_i\}) + \sum_i g_2^{\ i} (dn_i/dz)^2 - \mu_h n_h - \mu_c n_c].$$ (3)

The predicted behavior of the EHL surface profiles, as the phase separation is approached, is shown in Fig. 1. The parameter $\tilde{y}$ is defined by $\tilde{y} = (y - y^*)/y^*$, where $y = n_h/(n_h + n_c)$ is the hot-electron concentration, and y^* is the value of y at which the phase separation occurs. The electron-hole drop exists as a single homogeneous bulk phase for $\tilde{y} > 0$. However, as $\tilde{y} = 0$ is approached, a plateau begins to develop in the cold-electron surface profile. An indication of this is seen already for $\tilde{y} = 0.01$, and at $\tilde{y} = 0.001$ it is
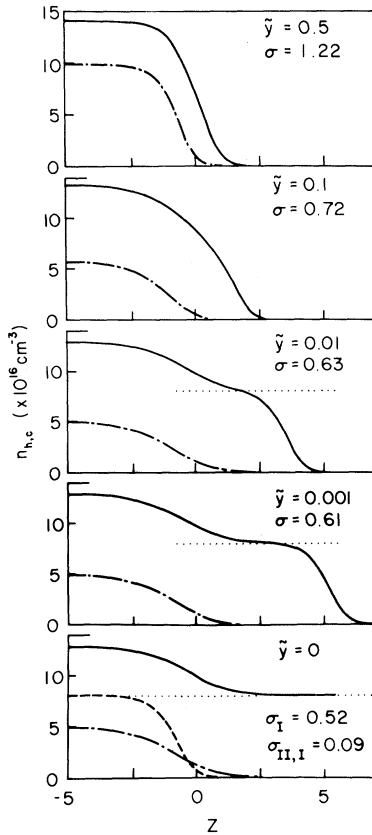
unmistakable. This plateau is a surface precursor of the new phase (phase I) which emerges as a *bulk* phase only when $\tilde{y} = 0$ is reached. The cold-electron density in the plateau region approaches the bulk density of phase I (which is indicated by the dotted lines) as $\tilde{y} = 0$ is approached. Concurrently the plateau broadens, and becomes the bulk phase I when its width reaches macroscopic size at $\tilde{y} = 0$.

A clear intuitive picture of the physics underlying this behavior can be obtained by studying the local free-energy density $\varphi(n_c, n_h) = g_0(\{n_i\}) - \mu_h n_h - \mu_c n_c$ which enters into the surface-energy integral (3).[11] The contours of constant φ are shown in Fig. 2 for the phase equilibrium case $\tilde{y} = 0$ of Fig. 1. φ vanishes where (n_c, n_h) corresponds to phase II (square), to phase I (circle), or to the vapor phase [which is the vacuum $(0, 0)$ at $T = 0$]. Notice that well-defined "valleys" in the free-energy density connect phase II to phase I and phase I to the vacuum but there is no other such valley connecting phase II to the vacuum directly. In order to minimize the energy of the surface of phase II, the local densities $[n_c(z), n_h(z)]$ must follow a trajectory from phase II to the vacuum which closely approximates the bottom of these valleys. Such a trajectory must pass through phase I. For other trajectories the surface energy would not be stationary
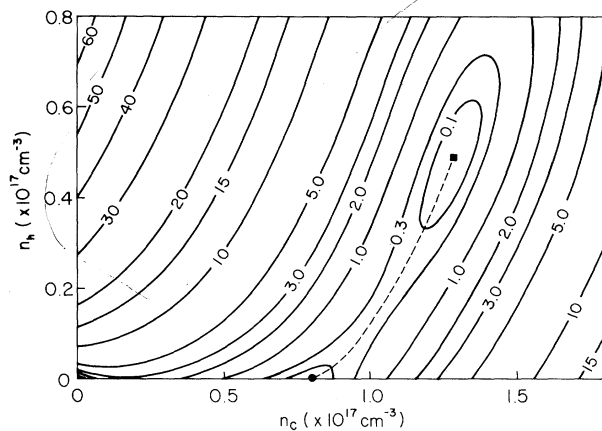

FIG. 1. Surface and interface profiles of n_c (solid lines) and n_h (dot-dashed) vs the coordinate z (units of a_B) normal to the surface, for a stress splitting of the valence band at $\vec{k} = 0$ of 2 meV. $a_B = 177$ Å. For meaning of $\tilde{y}$ see text. For $\tilde{y} = 0$ the solid and dot-dashed lines give the interface profile between phases II and I; the surface profile of phase I is dashed. For meaning of dotted lines see text. Surface and interface tensions are in 10^{-4} dyn cm^{-1}. The exchange-correlation energy values calculated for Ge(1,1) in Ref. 10 were used. The results using values for Ge(4,2) are similar but the surface energies are somewhat smaller.

FIG. 2. Contours of free energy density φ (in 10^{15} Ry cm^{-3}) plotted vs n_h and n_c for the case $\tilde{y} = 0$ of Fig. 1. The calculated trajectory in (n_c, n_h) space of the interface between phases II (square) and I (circle) is dashed. 1 Ry = 2.65 MeV.

against small variations of the path. Hence at $\bar{y} = 0$, phase II cannot have a surface which is not coated with at least a thin layer of phase I. Similar behavior is found for the other values of stress for which the EHL phase separates. Such situations have been described in chemical mixtures and the phenomenon is known as "perfect wetting."[1] The precision with which the actual calculated interface trajectory between phases II and I (dashed line, Fig. 2) follows the bottom of the valley is a striking manifestation of the accuracy of the above argument. If $\bar{y}$ is increased from zero, the contours of φ {and hence the trajectory $[n_c(z), n_h(z)]$} change continuously resulting in the series of profiles shown in Fig. 1.

The results presented here have direct experimental implications. The prediction that, at phase separation, phase II should always be completely coated with a layer of phase I provides the first theoretical justification of the "coated sphere model" which has been used on an *ad hoc* basis by Timusk and Zarate to interpret their plasmon absorption experiments.[5] Also the prediction that as the phase separation sets in, phase I grows continuously out of a surface precursor which appears prior to phase separation implies that the phase separation process occurs without nucleation having to take place. This means that there should be no hysteresis effects associated with the phase separation, in marked contrast with the process of formation of the EHL itself from the exciton gas.[7] This result is of crucial significance for any quantitative interpretation of time-resolved photoluminescence experiments studying the phase separation, such as those of Bajaj, Tong, and Wong.[4] In these experiments a laser pulse creates an EHL with a high concentration y of hot electrons. Then y gradually decreases as a result of decay processes and eventually is low enough for the phase separation to take place. Time-resolved luminescence spectra are taken in order to observe this phase transition. A direct experimental test of whether hysteresis occurs could be made in a two-pulse experiment, in which the second pulse could be used to reverse the phase separation process by raising the concentration of hot electrons in the EHL.[12]

Because of the gradient expansion of the energy used in (1), the present calculations omit the small Friedel oscillations which occur at EHL surfaces.[13] However, it seems very unlikely that including such effects would seriously modify the physics contained in the topography of Fig. 2 which is responsible for the predictions made in this article.

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[11]A similar argument has been used to explain the Cahn transition in chemical mixtures although actual maps of the free energy density could not be calculated for the systems involved.

[12]It should be emphasized that the phase transition which is studied in this article and which has been the subject of experiments (Ref. 4) is phase II ⇌ phase II + phase I. A different phase transition, namely, phase I ⇌ phase I + phase II can also occur in this system if hot electrons are added to phase I. Hysteresis is to be expected in the latter phase transition, in contrast with the present prediction of no hysteresis in the former one.

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